Solicited Proposal for

Task 3.2
of
"Initial Data Analysis of CRPAQS Field Program Measurements"

California Regional $PM_{10}/PM_{2.5}$ Air Quality Study

Submitted to:

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Modeling & Meteorology Branch
Planning & Technical Support Division
California Air Resources Board
Program Manager
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December 14, 2001

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1. INTRODUCTION

1.1 Goals and Objectives

CRPAQS provides a rich data base that can be used to better understand how central California air quality networks can be used for more purposes than just compliance. Owing to the complexity of the air quality problems in central California, CRPAQS will not be the final air quality study, and it is important to record what was learned in terms of network requirements. Many of the scientists participating in CRPAQS may not be available for this work a decade into the future. There are also other monitoring purposes that are useful and important that need to be considered in network design.

The objectives of Task 3.2 are to:

- Examine diurnal variations of hourly PM mass, nitrate, black carbon, and particle light scattering measurements.
- Evaluate spatial patterns of continuous $PM_{2.5}$ mass, nitrate, sulfate, black carbon, organic (or total) carbon, and particle light scattering measurements at the anchor and satellite sites.
- Evaluate effects of sampling duration/frequency on annual and 24-hour standard attainment.
- Establish a framework for optimal temporal and spatial resolution in a compliance monitoring network.

This task requires the results of Task 1.1 and Task 3.1. It will provide input to Task 1.2.

1.2 Background

Ambient and workplace air quality measurements are made for several purposes, and these purposes influence sampling locations, durations, frequencies, variables measured, and number of samples needed to represent a population.

- **Compliance with Air Quality Standards:** Ambient air quality standards have been established for ambient air in the United States and elsewhere (U.S. EPA, 1997). Indoor air standards are available for industrial workplaces (Samet and Spengler, 1991; Yocom and McCarthy, 1991) but are not common for household and office air. A critical need for particle measurements is to determine if a location is in compliance with an existing standard and to determine if trends show improvements in air quality. For this purpose, precision of the measurement by the variety of indicators in use is the most important consideration. Comparisons of various potential indicators, under a variety of atmospheric and air quality conditions are essential. PM standards for ambient air are currently

based on 24-hour measurements, with measurements typically taken every sixth day being used to estimate an annual average. Compliance monitoring often requires long-term monitoring over many years, depending on the form and values of the standards. Since public policy, financial or criminal penalties, or litigation result from these measurements, they must be well documented and of unquestionable quality.

- **Alerts:** Indoor or outdoor pollution levels approaching or exceeding concentrations that cause immediate and adverse health consequences require decisions to issue public warnings, use respirators, or to evacuate. In-situ continuous monitors with fast response times are needed for alerts. High accuracy and precision are not needed, as long as a high danger threshold can be quickly detected. The data returned by alert networks must be monitored, either automatically or manually, to sound an alarm. Smoke and carbon monoxide detectors are commonly employed in homes for this purpose. Confined workplaces often contain oxygen or poisonous gas monitors. Air pollution control agencies in many urban areas telemeter their continuous ambient measurements to central locations and publish a pollution index or warnings to stay inside or reduce outdoor physical activity. While quantitative continuous, real-time monitors have been used for several gaseous pollutants, they are only recently available for particle measurements and have not been completely perfected for this purpose (Watson et al., 1998a). For alerts, large measurement uncertainties and detection limits can be tolerated, as can crude measurement methods, as long as these methods immediately indicate exceedance of a high concentration in the vicinity of a susceptible population.

- **Implementation of a Standard:** To develop strategies to reduce pollution in order to attain a standard, measurements are needed that identify source categories and permit the development and validation of air quality models. For these purposes, PM parameters other than mass, such as chemical composition and size distribution, must be measured. Measurements are needed with shorter time resolution to observe changes in pollution associated with diurnal changes in emissions and the boundary layer. The causes of excessive concentrations that result in alerts or non-compliance are not always evident. Additional measurements are often needed to identify and quantify contributions from excessive emitters so that effective measures can be implemented. Emissions control strategies may take years to complete in a large airshed, and long-term monitoring is often needed to evaluate their effectiveness.

- **Atmospheric Process Research:** Excessive particle concentrations result from complex interactions among emissions and meteorology. Much of this science is still unknown, especially that related to the constituents and sources of secondary aerosol that is formed from gases. Networks for process research require simultaneous measurements at the surface and aloft with novel measurement devices. These networks are usually operated for a few days or weeks during pollution episodes. Source evaluation and atmospheric process research require accurate measurements of many observables taken simultaneously at many

locations. The expense and complexity of such measurements often limits them to specific episodes that can be analyzed or modeled in great detail.

- **Determination of Health Effects:** PM measurements are needed to determine exposure for use in epidemiological studies, to assess exposure for risk assessment, and to determine components of PM that guide planning and interpretation of toxicologic experiments. For these purposes size and chemical composition may be needed. For exposure assessment, different measurement time intervals may be needed. For acute epidemiology, one-hour or continuous measurements may be needed as well as 24-hour measurements. For chronic epidemiologic studies, measurements that integrate over a week to a month may be more cost-effective than hourly or daily concentration averages. For dosimetric studies and modeling, particle size distributions and the behavior of particles as relative humidity and temperature are increased to those in the respiratory system are required. Health outcomes are affected by non-pollution variables that are often unquantified. A variety of observables need to be measured to separate individual and interactive effects of these observables on health outcomes.

- **Determination of Ecological Effects:** Chemical concentrations in rain, fog, and dew are needed to understand the contributions of PM to soiling of surfaces, damage to materials, and wet and dry deposition of acidity and toxic substances to surface water, soil and plants. Some differentiation into particle size is needed to determine dry deposition.

- **Determination of Radiative Effects:** Particles reduce visibility by scattering and absorbing light. They also have a direct effect on the climate by scattering visible and ultraviolet light back into space and indirectly, as cloud condensation nuclei, by changing the albedo and stability of clouds. For understanding these effects information is needed on refractive index (including ratio of scattering to absorption), size distribution, and change in particle size with change in relative humidity.

The CRPAQS data set contains a unique set of measurements for determining how a network can meet several of these needs simultaneously. For the first time, semi-continuous particle composition data were collected simultaneously at multiple sites within the San Joaquin Valley. This temporally and spatially resolved data set includes $PM_{2.5}$ mass, nitrate, particle light absorption (black carbon), and dry particle light scattering measured with 5- or 10-minute time resolution at ten anchor sites (Bethel Island, Walnut Grove, San Jose–Fourth St., Sacramento, Sierra Foothill, Fresno, Corcoran, Angiola, Bakersfield, and Edwards AFB), as well as continuous measurements of $PM_{2.5}$ organic carbon, elemental carbon, and sulfate at the three annual anchor sites (Fresno, Angiola, and Bakersfield). These data provide insights into variations throughout the San Joaquin Valley. Additionally, spatial variability is expressed in data collected through the CRPAQS network, which has 5-minute particle scattering data from 32 locations in the anchor and satellite networks where 24-hour $PM_{2.5}$ and/or PM_{10} mass and chemical composition were acquired, and from 38 additional locations (during different periods) with only nephelometer measurements. Table 1.1-6 of DRI's

proposal for Task 1.1 summarizes the locations and sampling periods for these measurements.

Each of these parameters provides a different insight into the question of Task 3.2. Nitrate and black carbon are both important contributors to $PM_{2.5}$ mass, but their origins are different. Nitrate is a secondary constituent formed in the atmosphere by chemical transformation of nitrogen oxides. Black carbon is a primary constituent emitted directly into the atmosphere by various combustion sources. It will be important to evaluate how temporal and spatial variations of these two constituents compare to those for $PM_{2.5}$ mass, as this is the parameter subject to regulation. Additionally, spatial variability among the anchor sites can be compared to spatial variability among sites in regional satellite network. Daily profiles for these constituents will be compared to those for $PM_{2.5}$ mass, nitrate, and black carbon. Comparisons will be made with the 5 times/day winter episode measurements where additional chemical constituents will be examined. Finally, the results of the analyses will be synthesized to directly answer the question posed, namely what information is lost as averaging times are increased, or as the number of sites is decreased.

1.3 Evaluation Criteria

The combination of staff, current research projects, facilities, and cost structures of the Desert Research Institute (DRI) and Aerosol Dynamics Inc. (ADI) will make this proposal especially attractive to the Technical Committee. The evaluation criteria include: 1) technical approach, 2) expertise of the proposed staff, 3) related previous experience, and 4) cost-effectiveness.

The technical approach is presented in Section 3 of this proposal. This approach provides an overview of concurrent continuous mass and chemical measurements and their diurnal patterns using black carbon and nitrate, respectively, to represent primary and secondary constituents of $PM_{2.5}$. $PM_{2.5}$ mass and particle light scattering measurements from the satellite network during annual, summer, fall, and winter sampling periods will be used to examine spatial variations. Optimizing sampling frequency and balancing spatial and temporal resolution will be discussed.

The principals proposed for DRI are unsurpassed in terms of their demonstrated expertise in this type of study. Dr. Judith Chow at DRI has been a major participant in many California air quality studies including:

- *In California's central valley:* the 1988-89 Valley Air Quality Study (VAQS; Chow et al., 1992b, 1993), 1990 San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions, and Experiments (SJVAQS/AUSPEX; Fujita et al., 1995; Chow et al., 1996b), 1995 San Joaquin Valley Integrated Monitoring Study (IMS95; Chow et al., 1998), 1999-2001 CRPAQS aerosol measurements, and 1999-2003 Fresno Supersite Study (Watson et al., 2000; Watson and Chow, 2001a, 2001b);

- *Along the Pacific coast of California:* the 1989 Santa Barbara PM_{10} Study (Chow et al., 1996a) and 1991-92 Bay Area PM_{10} Study (Chow et al., 1995); and

- *In southern and southeastern California:* the 1987 Southern California Air Quality Study (Chow et al., 1994a, 1994b; Fujita et al., 1994; Watson et al., 1994), 1988 Rubidoux/Riverside Neighborhood-Scale Study (Chow et al., 1992a), and 1992-93 Imperial Valley/Mexicali PM_{10} Study (Chow et al., 2000; Chow and Watson, 2001; Watson and Chow, 2001c).

The selected peer-reviewed references attest to her past experience and qualifications.

Dr. Susanne Hering, president of ADI, has more than 25 years of experience in aerosol measurements. She is one of the principal developers of an automated system for high-time resolution measurements of fine particulate nitrate and sulfate. This system was used in CRPAQS and is deployed at many of the EPA supersites. Recently ADI developed a cascaded version of this instrument that is deployed at the Los Angeles supersite to provide continuous nitrate measurements in three size fractions.

DRI's and ADI's staff have extensive experience in performing spatial and temporal analysis. The principal investigators and the supporting staff are well acquainted with the sampling and analysis aspects of the proposed study. The proposed team demonstrates experience and participation in nearly every one of the major air quality studies conducted over the past two decades. The principal investigator's experience includes major roles in over a dozen major aerosol aerosol and visibility monitoring studies that have resulted in significant advances in the understanding of air pollution. Methods for data analysis are specified in the technical approach in Section 3.

The proponent's ability to carry out the proposed work within the time and budget constraints is outlined in Section 5. A key to maintaining the schedule is that DRI staff are well acquainted with the aerosol measurements taken in the San Joaquin Valley as well as the sampling site locations and surrounding environs. ADI is already a subcontractor to DRI for Fresno supersite research. Dr. Susanne Hering and her staff are responsible for the collection, evaluation, and analysis of continuous nitrate, sulfate, and particle size distribution data in Fresno. DRI scientists (Dr. Judith Chow, Dr. John Watson, Dr. Douglas Lowenthal, Dr. John Bowen, Mr. Steven Kohl, Mr. Matt Gonzi, Mr. Dale Crow) have been actively working on field operations, data analysis, and air quality modeling for the Fresno Supersite since May 1999. The objectives of the Fresno Supersite project are to: 1) test, evaluate, and compare non-routine and existing monitoring methods; 2) acquire data bases to evaluate relationships between aerosol properties, co-factors, and observed health endpoints; and 3) support regulatory agencies in the development of cost-effective emissions reduction implementation plans. The Fresno Supersite research, which is funded through a cooperative agreement with the U.S. Environmental Protection Agency (U.S. EPA) and the National Oceanic and Atmospheric Administration (NOAA), is directly related to the data analysis to be performed for CRPAQS; as such, substantial cost benefits can be achieved (as shown in Section 8) if DRI is awarded the CRPAQS data analysis task.

This project can and will be given priority. The key personnel, Drs. Chow and Hering, are fully dedicated to this project. They have been involved in air quality measurements in the San Joaquin Valley for more than a decade, and they have always placed this local interest above other more remote opportunities that have presented

themselves. In addition, DRI is a state agency and is backed by the University and Community College System of Nevada and the State of Nevada. DRI's financial stability as a unit of the University of Nevada System is healthy, long-term, and growing.

With respect to compensation for contracted services, DRI is a non-profit entity and records no financial gain from revenues collected from this or any other project. DRI's interest in this project derives from the unique opportunities it offers to advance our fundamental knowledge about the spatial scales represented by particle samplers. The project has been budgeted to take advantage of different cost structures of the project team. Though DRI must adhere to certain rules established by the Federal Government for cost recovery, it is amenable to alternative arrangements that reduce costs to the sponsors.

Finally, DRI, as part of the State University System, maintains a policy of non-advocacy. DRI participates only in the research aspects of air pollution studies. Results from these studies are presented objectively to decisionmakers without regard to the sensitivities of special interests or political pressures. DRI enjoys the reputation of working equally well with the U.S. EPA, various state and local agencies, and with commercial interests in the development of technical guidance and databases for regulatory analysis. Wherever possible, DRI collaborates with, rather than competes with, the private-sector environmental consulting industry to obtain the best combination of skills, lowest costs, and greatest benefit to the project sponsor and to DRI's goal of technology transfer between university research and environmental assessment.

2. SCOPE OF WORK

Task 3.2 of the Request for Proposal asks two questions:

- QUESTION 3.2-1 How frequent must measurements be acquired and with what duration to represent changes in mass and chemical concentrations throughout the day?

- QUESTION 3.2-2 How should temporal resolution be balanced with spatial resolution?

The following scope of work is structured to answer each of the questions as noted. Each of these subtasks supplies information to address primary **QUESTION 3: WHAT ARE THE TEMPORAL AND SPATIAL REQUIREMENTS FOR RESEARCH AND COMPLIANCE MONITORING NETWORKS?**

2.1 Task 3.2.1 – Diurnal Patterns

addresses: QUESTION 3.2-1. Measurement frequency and duration?

Daily profiles for $PM_{2.5}$ mass, nitrate, black carbon, particle light scattering coefficient will be characterized at the ten anchor sites where concurrent measurements were made. Several questions will be addressed. What are the average and 50th percentile (median) diurnal patterns for nitrate and black carbon at each of the sites? How variable is that pattern from day to day? How does the daily profile vary for different synoptic conditions? How do diurnal patterns for nitrate and black carbon compare to those for $PM_{2.5}$ mass as measured by beta attenuation monitor (BAM), and as indicated by total particle scattering (b_{sp}) data? These questions will be answered by examining several specific metrics that characterize the diurnal profile such as the time of day of maximum concentration, the half-width of the duration of the maxima, its relative magnitude, and whether a secondary maximum is present and its characteristics of time, half-width, and magnitude. Nitrate and black carbon are chosen for this detailed analysis because they have the most complete data set, and because they represent secondary and primary particulate species, respectively. $PM_{2.5}$ mass by BAM and particle light scattering (b_{sp}) by nephelometer are used because they are widely applied in the CRPAQS network, and because they are time-resolved estimators of the regulated parameter, $PM_{2.5}$ mass. Additional continuous measurements of sulfate, organic carbon, and total carbon collected at Fresno, Angiola, and Bakersfield will be examined as part of this task. Diurnal patterns of 5 times/day, filter-based mass and chemistry data acquired during 15 winter episode days at five anchor sites will also be examined and compared with hourly measurements.

2.2 Task 3.2.2 – Anchor Site Spatial Variations

addresses: QUESTION 3.2-2. Temporal resolution vs. spatial resolution?

The ten anchor sites with continuous $PM_{2.5}$ mass, nitrate, black carbon, and particle light scattering measurements are spread throughout the length of the San Joaquin Valley, and are ideally suited for evaluating simultaneous variability in diurnal patterns. The characteristics of diurnal variations in mass, nitrate, and black carbon concentrations will be compared. The data will be stratified by synoptic conditions. Periods of high concentrations and stagnation will be examined in detail to assess differences among sites in the time of day of the maximum concentration, the relative magnitude of the concentration peak, and its duration, as well as in average concentrations.

2.3 Task 3.2.3 – Satellite Site Spatial Variations

addresses: QUESTION 3.2-2. Temporal resolution vs. spatial resolution?

The representativeness of the central monitoring site to the local region will be evaluated through analysis of results from the satellite network. A successive moving average subtraction method will be applied to 5-minute particle light scattering measurements at the 70 satellite locations to detect short-term spikes of nearby small emitters and sites located within the urban plume but distant from specific emitters. This analysis will determine the extent of middle-scale (100 to 500 m), neighborhood-scale (500 m to 4 km), and urban-scale (4 to 100 km) influences upon a fixed monitor. For sites where nephelometers were not collocated with $PM_{2.5}$ samplers, nephelometer data will be evaluated with $PM_{2.5}$ measurements from nearby sites. This method will also be applied to other black carbon and nitrate measurements from Fresno, Angiola, and Bakersfield to separate regional, urban, and local sources of these components.

2.4 Task 3.2.4 – Sampling Frequency

addresses: QUESTION 3.2-1. Measurement frequency and duration?

Determine the extent to which short-duration (10-minute, 3-hour, 5-hour, and 8-hour) measurements can represent 24-hour-average concentrations. For 24-hour sampling in the compliance network, determine an adequate sampling frequency to represent human exposure. Perform statistical testing on various sampling frequencies to determine the number of samples required to obtain an adequate annual average.

2.5 Task 3.2.5 – Synthesis

addresses: QUESTION 3.2-1. Measurement frequency and duration?
QUESTION 3.2-2. Temporal resolution vs. spatial resolution?

The questions in Task 3.2 will be addressed by quantifying the loss of information as averaging time is increased and the spatial extent of measurements is decreased. The specific metrics identified will be reevaluated for longer averaging periods, and compared among sites. These metrics include not only average concentrations, but also the magnitude and duration of daily concentration peaks, the time of day of the maxima or time-period-integrated maxima in 5 times/day samples, and the presence or absence of secondary maxima, and if present, its characteristics. Such an analysis will allow the investigator to

select averaging periods and spatial extents depending upon the specific questions posed for the research or monitoring study at hand.

3. TECHNICAL APPROACH

As shown in Table 3.2-1, concurrent $PM_{2.5}$ mass, nitrate, sulfate, black carbon, and particle light scattering measurements were acquired at ten ground locations (Bethel Island, Walnut Grove, San Jose–Fourth St., Sacramento–Del Paso Heights, Sierra Foothill, Fresno, Corcoran, Angiola, Bakersfield, and Edwards AFB) and two elevated locations (Walnut Grove, 300 m AGL; and Angiola Tower, 100 m AGL) within the sphere of the central valley. $PM_{2.5}$ mass was measured by Met One 1020 beta attenuation monitor (BAM) with one-hour time resolution. $PM_{2.5}$ nitrate and sulfate were acquired by Rupprecht & Patashnick 8400N nitrate and 8400S sulfate monitors, respectively, with 10-minute time resolution. Five-minute-average black carbon measurements were made by Andersen AE30S multi-color aethalometer. Particle light scattering was measured by Radiance Research M903 nephelometer with smart heater (heating when relative humidity is above 65%). This simultaneously spatially and time-resolved particle composition is unique. It allows the direct answer to the questions of Task 3.2 through comparison of appropriate averages over time and space.

3.1 Task 3.2.1 – Diurnal Patterns

Key to this analysis is defining the metrics that best characterize the important aspects of the diurnal patterns for each of the constituents. This can be illustrated by the example shown in Figure 3.2-1 for daily patterns of nitrate concentrations measured at Fresno in October 2000. Ten-minute measurements are shown with 30-minute and 12-hour averages of the data. Clearly evident in the 10-minute and 30-minute averages is the morning maxima in nitrate concentrations that occurs between 0800 and 1000 PST. Less evident is a secondary, nighttime maxima occurring between 2100 and 0400 PST. The most straightforward manner to characterize the daily pattern is to compute the daily averaged profile, that is to average the data by time of day. This is shown in Figure 3.2-2 for nitrate, sulfate, and black carbon for the October 2000 period in Fresno. This figure clearly shows the midmorning maxima in the nitrate profile. It also shows the contrast with the black carbon, with two daily maxima occurring (a sharp peak in the morning and a broader peak in the evening). The nighttime nitrate maxima is not as evident, in part because it is not as pronounced, but also because the time of its occurrence varies by several hours from one day to the next. Little diurnal variation is found for sulfate, partially due to low ambient concentrations (<2 $\mu g/m^3$).

One way to characterize the overall time variability is by the variance in the data with respect to a longer-term average. For the data shown, the deviation of the difference between 30-minute averages and 10-minute averages gives a variance of 0.9 $\mu g/m^3$. This is close to the variability in the experimental measurement. By contrast, the variance between actual data and 12-hour averages is 5 $\mu g/m^3$. Indeed, the variance between actual and averaged data can be expressed as a function of the averaging period, as illustrated in Figure 3.2-3. This graph shows the standard error that could be anticipated in the actual concentration if represented by an average value with the averaging time shown on the ordinate.

Table 3.2-1. Summary of in-situ continuous measurements acquired at CRPAQS anchor sites.

Site Code	Site Name	$PM_{2.5}$		PM_{10}		Particle light scattering (Radiance M903 nephelometer)	$PM_{2.5}$ Organic and elemental carbon (R&P 5400)	$PM_{2.5}$ Particle light absorption (single- and seven-wavelength aethalometers)	$PM_{2.5}$ Nitrate	$PM_{2.5}$ Sulfate
		TEOM	BAM	TEOM	BAM					
ANGI	Angiola		A		A	A[a]	A	A	W[a]	W
BAC	Bakersfield		A		A	A	A	A	W	W
BTI	Bethel Island		W			A		W	W	
COP	Corcoran		F		F	F		F	F	
EDW	Edwards AFB		S		S	A		S		
FSF	Fresno	A	A	A	A	A	A	A	A*	A
SDP	Sacramento–Del Paso Heights		W			A		A		
SJ4	San Jose–Fourth St.		W			A		A	W	
SNFH	Sierra Foothill		W			A		W	W	
WAG	Walnut Grove					A		W	W[b]	

A = Data available from the annual sampling program between 12/01/99 and 02/03/01.

W = Data available from the winter intensive study period between 12/01/00 and 02/03/01.

F = Data available from the fall intensive study between 10/10/01 and 11/14/01.

* = Collocated measurements at ground level.

[a] Measurements at the Angiola site were taken both at ground level and at a location elevated 100 m above ground level.

[b] Measurements at the Walnut Grove site were taken both at ground level and at a location elevated 300 m above ground level.

Figure 3.2-1. Diurnal variations of $PM_{2.5}$ nitrate concentrations between 10/15/00 and 10/20/00 at the Fresno site. Dots represent 10-minute averages. The lighter solid line represents 30-minute averages. The heavier solid/dashed line represents 12-hour averages.

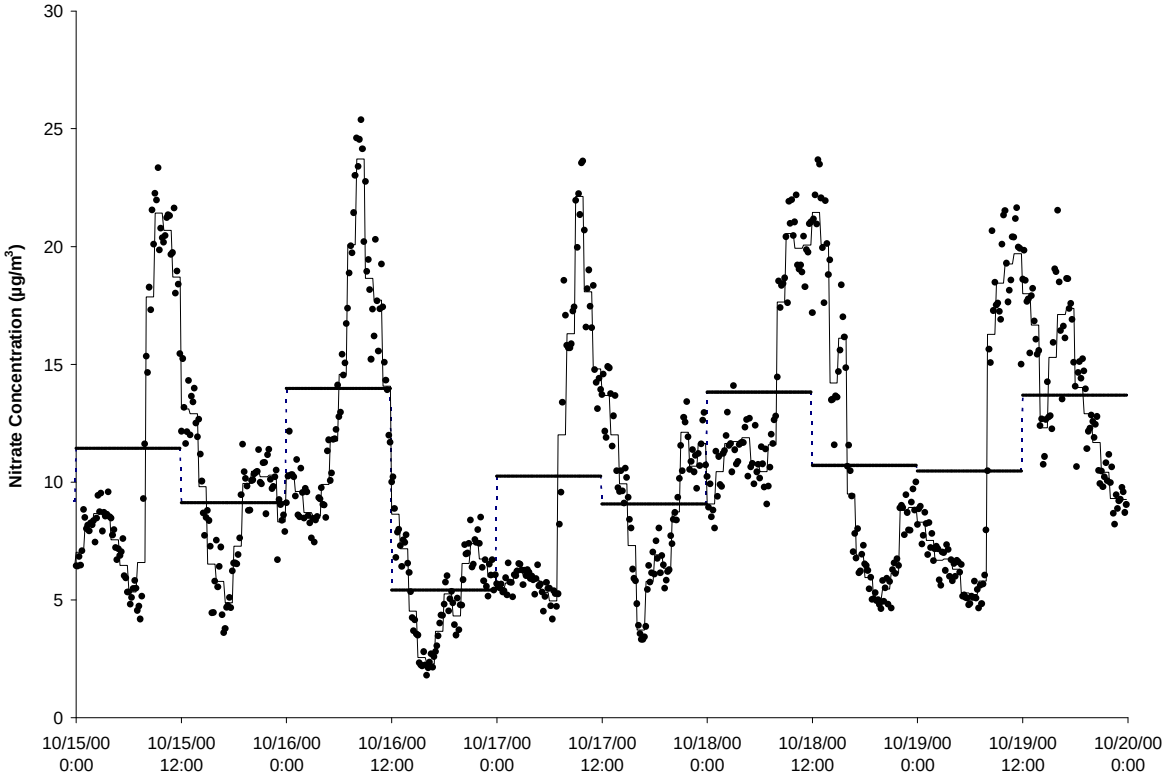


Figure 3.2-2. Diurnal variations of 10-minute $PM_{2.5}$ nitrate and sulfate along with black carbon measurements averaged over the sampling period between 10/05/00 and 10/20/00.

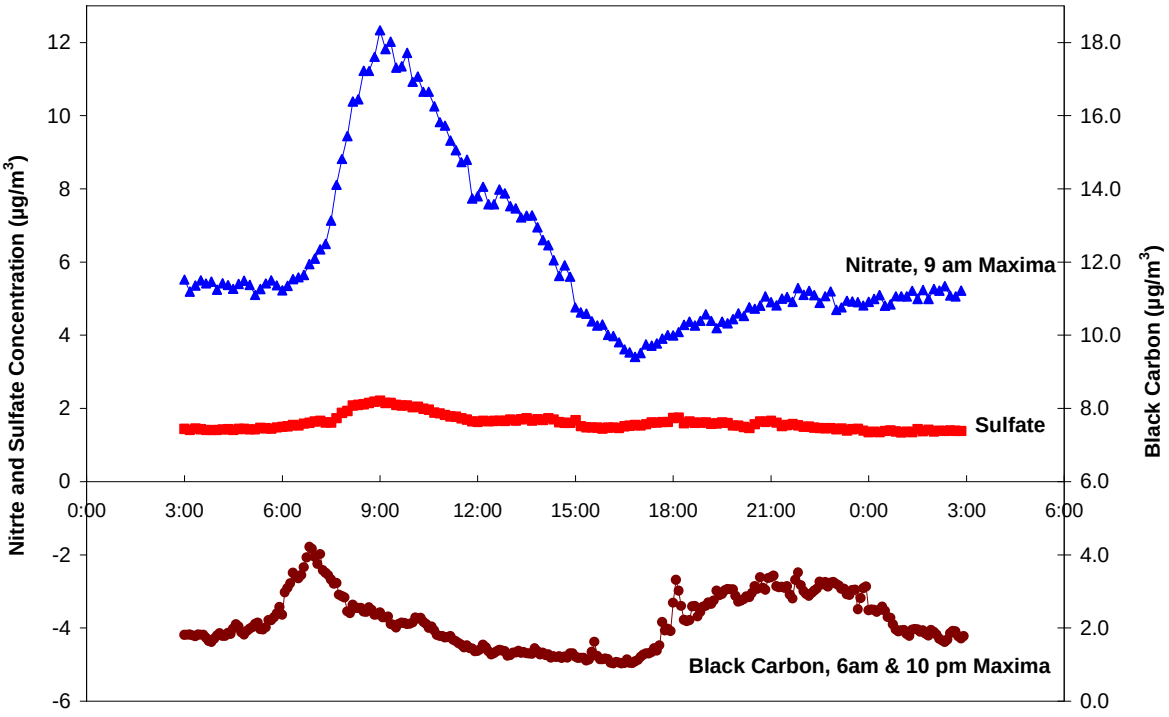
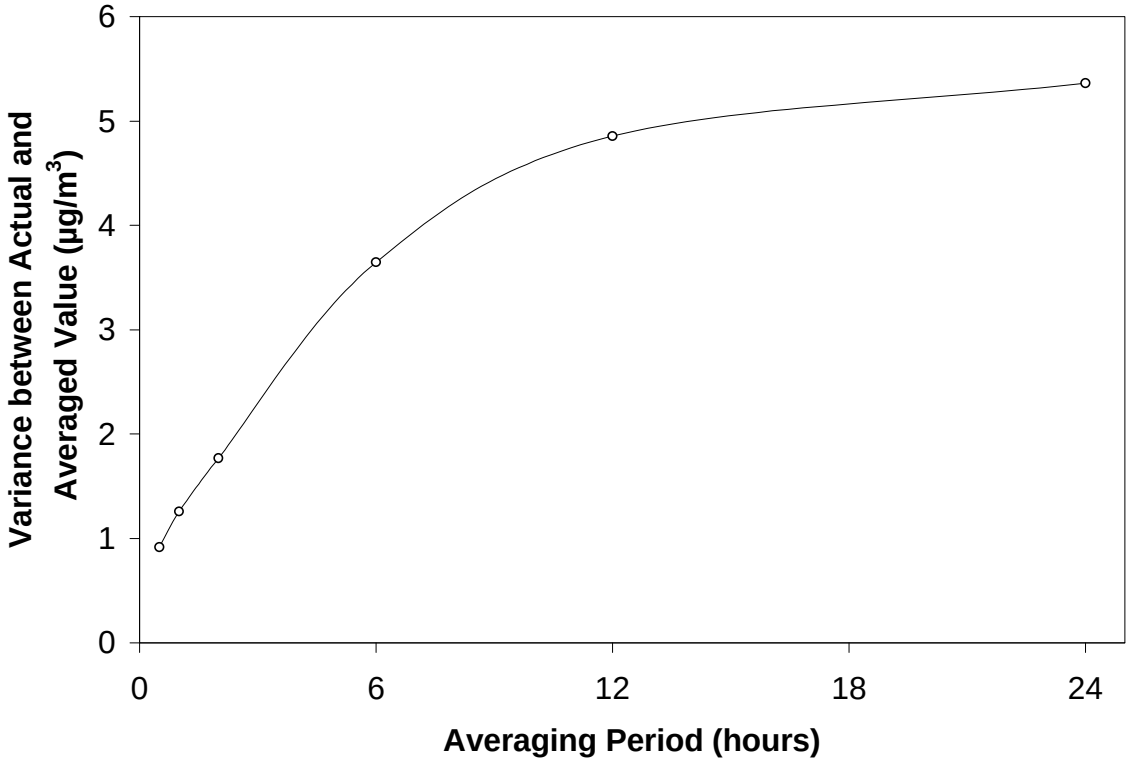


Figure 3.2-3. Differences in variance as a function of average sampling duration for 10-minute nitrate data acquired between 10/05/00 and 10/20/00 at the Fresno site.



Characterizing the overall variability does not capture information about the time of day of the concentration maxima, nor the width, or duration of the local concentration maxima. This is important information for understanding formation mechanisms or sources. For example, the black carbon morning and afternoon maximum shown in Figure 3.2-2 is consistent with a pattern that would be expected for vehicular source emissions. The time of day of the nitrate maxima has been used to infer the mechanism for nitrate formation, whether dominated by daytime gas phase or nighttime heterogeneous chemistry (Pun et al, 2001). Inspection of Figure 3.2-1 shows that the 12-hour average of the data starting at midnight does not accurately capture the time of day of the nitrate maximum. Certainly it would not capture the double peak that characterizes the black carbon profile. Thus this task will further characterize the daily profiles by examining the time of day of maximum concentration, the duration of that concentration peak, its relative magnitude, whether a secondary maximum is present, and if present, its characteristic time, duration, and magnitude. The duration of the concentration peak will be quantified through the width, in time, of the concentration peak at half-maximum concentration. Both the half-maximum concentration and the magnitude will be defined with respect to a baseline concentration value on either side of the concentration peak. The metrics that will be used are:

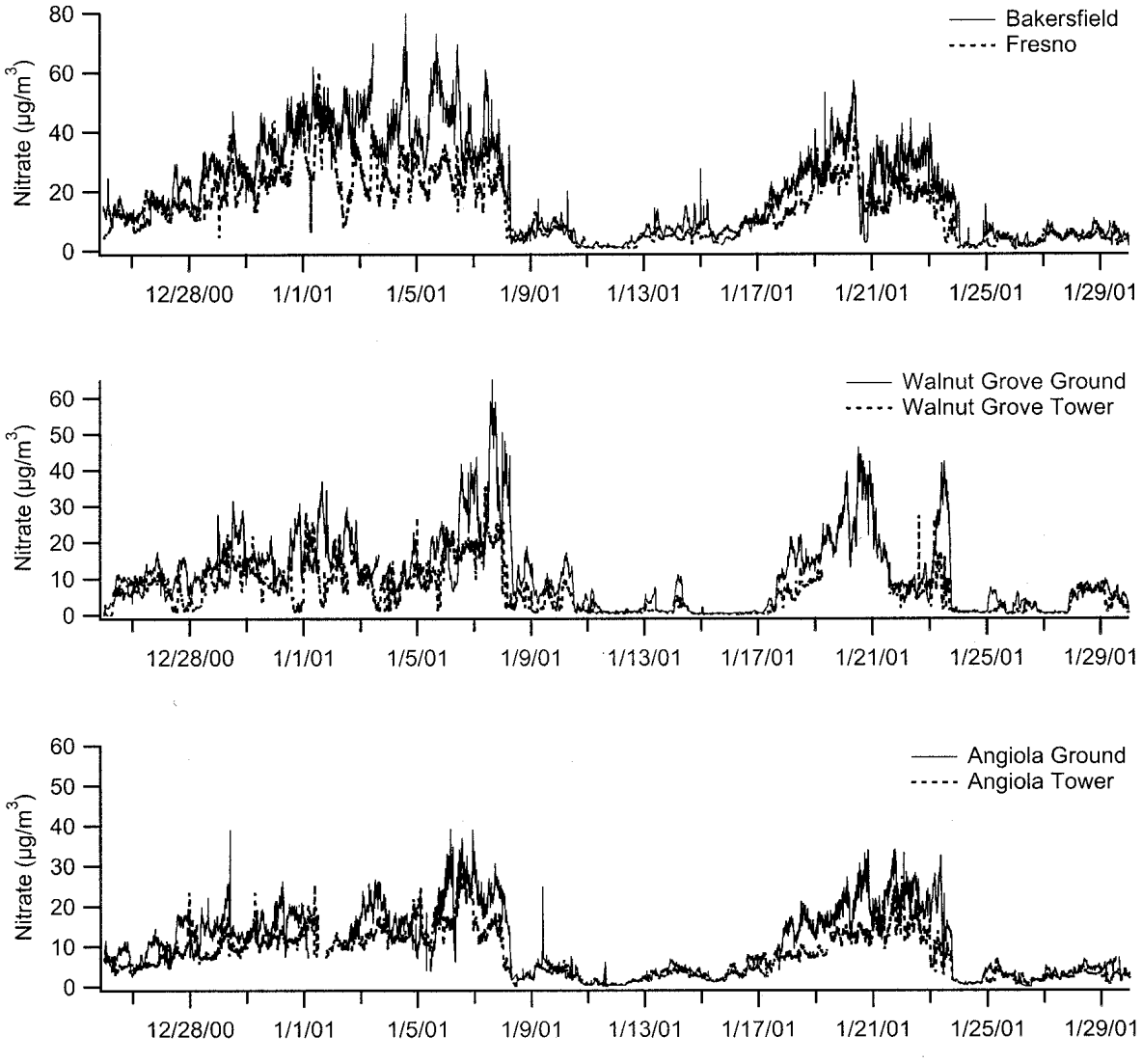
- Average concentrations for each 10-minute, 30-minute, hourly, 6-hour, 12-hour, and 24-hour period.
- Variance between actual and time-averaged concentrations.
- Time of day of concentration maximum.
- Duration of concentration maximum.
- Duration of concentration maximum at half-height.
- Relative magnitude of concentration maximum.

These metrics will be used to characterize diurnal profiles for $PM_{2.5}$ mass, nitrate, black carbon, and particle light scattering at each of the seven sites for which all four measurements are present. Note that these metrics can be calculated individually for each day of measurements. The daily profile for each chemical specie will be characterized by their mean profile, as shown in Figure 3.2-2, and by the standard deviation in the parameters that characterized the profile.

3.2 Task 3.2.2 – Anchor Site Spatial Variations

Anchor site spatial variations for particles in the San Joaquin Valley are illustrated by the concentration profiles for nitrate, shown in Figure 3.2-4 (Hering et al., 2001). Data are shown for the period from December 26, 2000, through January 30, 2001, at six locations (Fresno, Bakersfield, Angiola [at ground level and at 100 m above ground level, AGL], and Walnut Grove [at ground level and at 300 m AGL]). There is a similar overall pattern among

Figure 3.2-4. $PM_{2.5}$ nitrate measurements acquired at the Walnut Grove (at ground level and at 300 m above ground level), Fresno, Angiola (at ground level and at 100 above ground level), and Bakersfield sites between 12/26/00 and 01/30/01.



all sites. Multiday periods of elevated nitrate concentration are observed concurrently at all of the sites, with the largest values at the southernmost site (Bakersfield). A period of low nitrate is observed throughout these sites in early January. These large scale changes are certainly driven by meteorology, with near simultaneous occurance of either storms or staganation throughout the valley.

A strong diurnal pattern at each site is superimposed on the multiday pattern, as discussed in Task 3.2.1. The two urban sites (Bakersfield and Fresno) tend to show a midday maxima, although evening maxima are also observed. Maxima at the non-urban sites (Walnut Grove and Angiola) most often occur in the evening or early morning. The nighttime maxima are most pronounced for the elevated tower measurements at these sites and may indicate the importance of heterogeneous formation mechanisms for nitrate.

To evaluate spatial differences, the data will be stratified by meteorological regime, separating periods of stagnation from periods of stormy weather. For each of the meteorological regimes, the daily mean concentration profiles will be compared among the sites for $PM_{2.5}$ mass, nitrate, black carbon, and particle light scattering. The differences among the five sites will be quantified in terms of the metrics discussed at the end of Section 3.1 above. The analysis will examine whether each of the sites exhibits a single daily maximum or multiple concentration maxima, how the time of day of the primary maxima varies among the sites, and how the duration and magnitude of the maxima vary among sites. Whether differences are statistically significant will be examined using a nonparametric test such as the Friedman analysis of variance.

3.3 Task 3.2.3 – Satellite Site Spatial Variations

Spatial patterns of particle light scattering measurements at the 32 satellite sites collocated with $PM_{2.5}$ and/or PM_{10} filter measurements, as well as at 38 sites with only nephelometer measurements, will be examined in the same manner as at the anchor sites. Typical traces of particle light scattering concentrations for weekdays/weekends, different seasons, and episode days or periods will first be examined. The duration and magnitude of the primary and/or secondary maxima under different synpotic scales or surface meteorology characteristics will be sought.

Spectral analysis (Perrier et al., 1995; Hies et al., 2000), intervention analysis (Jorquera et al., 2000), and trend analysis (Somerville and Evans, 1995) models have been used to resolve complicated temporal spectra into linear and non-linear combinations of recurring patterns. A successive moving average subtraction will be used here with particle light scattering measurements from the 70 satellite sites to illustrate the method because it appears to be equally valid, is simple to understand, and can be easily implemented using common spreadsheet functions. This method can and should be compared with other time series methods to determine their differences or equivalence (Watson and Chow, 2001a).

In the successive moving average subtraction method, hourly average of 12 values surrounding a given 5-minute period is calculated and compared to the 5-minute value for that period. If the hourly average is less than the 5-minute value, the hourly average is

retained; if the hourly average is more than the 5-minute average, the 5-minute average is retained. The next step calculates 30-minute averages for this new data set and compares these to the 5-minute averages, with the new average retained unless it exceeds the 5-minute average. This process is applied one more time for a 15-minute average to obtain the baseline on which the short-duration pulses are imposed. Watson and Chow (2001b) demonstrated that short-duration pulses in 5-minute black carbon concentrations that are caused by nearby sources can be used in urban areas to estimate middle-scale (100 to 500 m), neighborhood-scale (500 m to 4 km), and urban-scale (4 to 100 km) source contributions. This technique will be compared with spatial patterns found in every-sixth-day, filter-based measurements from the CRPAQS satellite network.

3.4 Task 3.2.4 – Sampling Frequency

Chow (1995) observed that U.S. particulate standards are based on health relationships with measurements acquired from networks designed to determine compliance with previous standards. For suspended particles, this practice has perpetuated 24-hour filter sampling that does not recognize some of the potentially high short-term concentrations that may be a hazard. Shorter-duration measurements that are collocated with long-duration measurements for a limited time are needed to evaluate the extent to which the longer-duration measurements are achieving their desired objectives.

In Figure 3.2-5, the data from everyday $PM_{2.5}$ sampling during the winter 1999-2000 period show that many episodes are missed by every-sixth-day monitoring, although quarterly averages and frequency of U.S. air quality standard exceedances are adequately estimated. Long-term averages need less frequent samples than monitoring for extreme events. Table 3.2-2 compares the annual average and standard deviation, highest, second-highest, and several upper percentiles of 24-hour $PM_{2.5}$ concentrations for samples taken at daily and 2-, 3-, 6-, 12-, and 30-day intervals, using year 2000 as an example. U.S. $PM_{2.5}$ standards require sampling frequencies of every day to every sixth day, with more frequent sampling in communities with concentrations near or in excess of the standard.

Table 3.2-2 shows that annual averages for $PM_{2.5}$ are reasonably consistent with sampling frequencies up to 1 in 6 days or even 1 in 12 days, but at least for this particular urban sampling site, the maximum and second-highest concentrations are very sensitive to sampling frequency regardless of lag time between samples. The upper percentiles also have the possibility of significant error, especially when relatively few samples are available. The U.S. $PM_{2.5}$ and PM_{10} air quality standards are expressed in terms of percentiles over three-year intervals to increase the reliability of the measurement. If values for maximum concentrations are desired, however, sampling frequencies must be continuous and complete. Extreme values are rare events that do not always obey standard statistical distributions (de Nevers et al., 1977). These generalizations from Table 3.2-2 for $PM_{2.5}$ are consistent with those found from other locations and time periods (Watson et al., 1981). Similar analyses will be conducted to compare all available daily $PM_{2.5}$ measurements from the central valley backbone sites to determine adequate sampling frequency.

Figure 3.2-5. Daily, 24-hour average $PM_{2.5}$ concentrations at the Fresno Supersite (FSF) during winter 1999-2000. Light-shaded bars correspond to the U.S. EPA sixth-day sampling schedule and demonstrate that multi-day episodes are not represented by sporadic sampling.

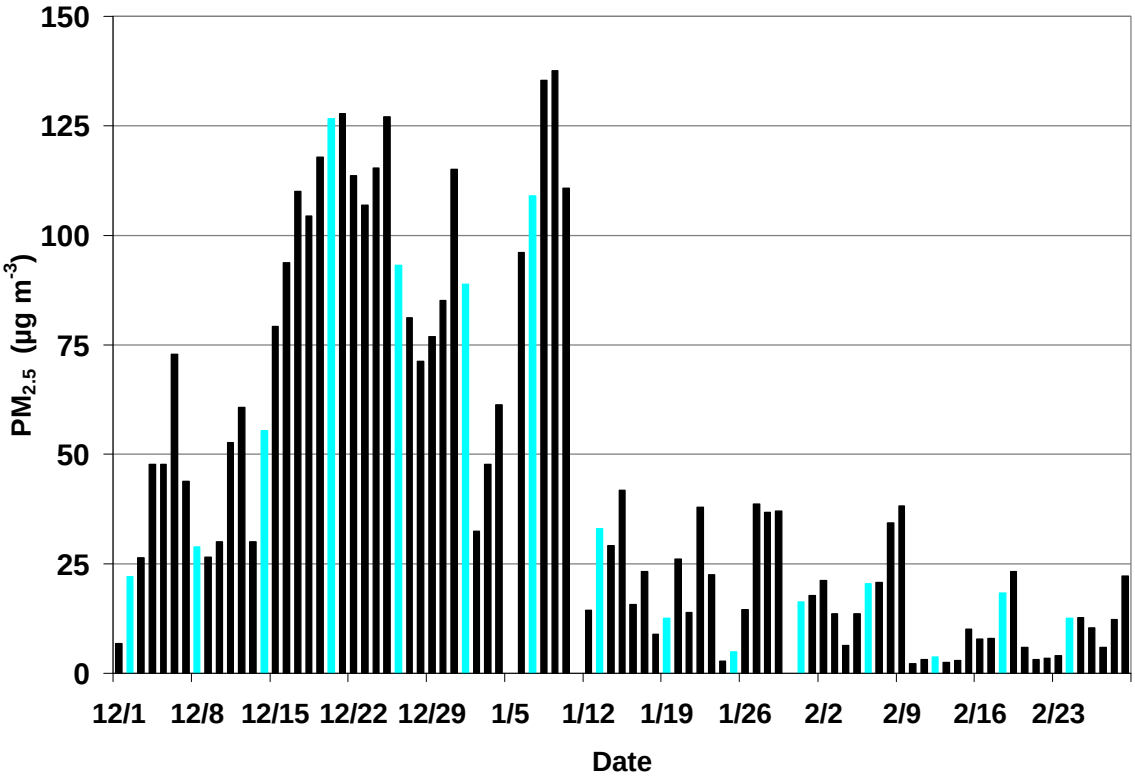


Table 3.2-2. Effects of sampling frequency on statistical indicators for 24-hour $PM_{2.5}$ concentrations (year 2000 data from the Fresno, Angiola, and Bakersfield sites).

	Annual Average	Standard Deviation	Minimum	Maximum	Second Maximum	99th%	98th%	95th%	90th%	Number in Average
FRESNO										
Every Day	19.6	22.6	1.7	137.6	135.5	109.9	96.0	68.7	46.4	351
Second Day	19.2	22.0	2.2	137.6	109.0	98.3	91.4	69.9	44.8	176
Third Day	20.6	23.1	1.7	110.8	109.0	107.0	94.4	74.8	54.0	118
Sixth Day	20.8	24.5	3.7	109.0	88.8	97.3	88.5	81.0	68.6	59
Twelfth Day	21.5	24.1	5.0	88.8	86.9	88.2	87.7	81.1	69.1	30
Thirtieth Day	26.1	28.0	6.6	88.8	73.9	87.1	85.5	80.6	71.1	12
ANGIOLA										
Every Day	17.9	17.0	1.0	99.2	98.4	84.2	78.1	50.6	39.8	265
Second Day	17.3	15.8	1.0	98.4	80.2	76.1	60.8	49.4	37.7	132
Third Day	17.7	17.2	1.0	98.4	82.8	84.4	78.9	49.5	35.9	91
Sixth Day	16.9	16.6	1.0	98.4	50.5	77.3	56.2	48.3	31.6	45
Twelfth Day	19.4	20.0	4.9	98.4	50.5	87.8	77.3	48.8	33.0	23
Thirtieth Day	19.8	14.1	7.9	50.5	34.4	49.2	47.9	44.0	37.6	9
BAKERSFIELD										
Every Day	23.4	19.7	3.5	114.7	98.4	91.0	82.8	71.5	49.0	341
Second Day	23.3	19.3	3.5	94.6	80.2	87.4	81.7	68.3	49.2	170
Third Day	23.0	19.0	4.2	92.8	82.8	86.4	80.3	67.5	46.2	113
Sixth Day	23.1	20.4	4.2	87.1	50.5	83.8	79.7	68.3	61.1	57
Twelfth Day	22.4	18.7	6.1	81.2	50.5	77.6	74.0	66.0	46.2	29
Thirtieth Day	23.7	20.3	6.1	68.3	34.4	67.6	66.9	64.9	57.4	13

Statistics for different averaging times (5-minute, 30-minute, 1-hour, 6-hour, 12-hour, 24-hour, monthly, seasonal, and annual averages, minima, maxima, 5th percentiles, and 95th percentiles) of continuous $PM_{2.5}$ mass, nitrate, black carbon, and particle light scattering measurements will be examined with the metrics discussed at the end of Section 3.1 above. These analyses and statistical results will determine: 1) the extent to which high concentrations are greatly attenuated over longer averaging times, and 2) the optimal averaging interval that is most representative for a given measurement.

Days with elevated concentrations will be examined separately. An example of a time-series material balance is shown in Figure 3.2-6 for continuous measurements acquired on December 26, 2000, with a daily average $PM_{2.5}$ mass of 93.5 $\mu g/m^3$. Hourly $PM_{2.5}$ BAM mass was lowest (40 to 45 $\mu g/m^3$) during the morning period between 0400 and 0900 PST, with a small increase from 1100 to 1200 PST partially due to an increase in nitrate concentrations. $PM_{2.5}$ mass, ammonium nitrate, and carbon all increased after 1700 PST and persisted through the night. Note that $PM_{2.5}$ TEOM mass was lower than the sum of carbonaceous aerosol and ammonium nitrate for most of the day except during the nighttime period, which indicates that much of the TEOM mass is lost when the sampling air is heated to 50 °C. Similar comparisons of concurrent continuous mass and chemical measurements will provide insight on the causes of elevated 24-hour concentrations.

3.5 Task 3.2.5 – Synthesis

Task 3.2 is charged with answering the questions of what frequency, what measurement duration, and what spatial resolution is needed to represent changes in particle mass and chemical concentrations. This task is designed to partially address a larger question (labeled Question 3) given as "What are the temporal and spatial requirement for research and compliance monitoring networks?" The specific answer to Question 3 will depend upon the research and monitoring objectives of the study at hand. The question that can be answered from the analyses in Task 3.2 is, "What information is lost as averaging times are increased, or as the number of sites is decreased?"

The questions of Task 3.2 will be answered in three ways. First, specific examples from the CRAPQS data set will be given. Second, differences among sites will be illustrated with averaged diurnal profiles for PM components stratified by location and meteorological regime. Third, the manner and extent to which the metrics discussed at the end of Section 3.1 are lost when averaging times are lengthened, or sampling is not as frequent, or fewer sites are included, will be quantified.

Watson and Chow (2002) examined a wintertime episode between 01/02/00 and 01/12/00 using 5-minute to 1-hour continuous measurements of mass, nitrate, black carbon, particle-bound polycyclic aromatic hydrocarbons (PAH), and meteorology. Figure 3.2-7 shows that black carbon and PAH decreased with $PM_{2.5}$ throughout the early morning, but increased slightly at 0700 and 1000 PST, as did CO and NO (not shown in this figure), even though $PM_{2.5}$ decreased. Nitrate decreased after 0700 PST until 0920 PST, when it abruptly increased from 30 to 52 $\mu g/m^3$ when the surface temperature passed 4 °C. Black carbon

Figure 3.2-6. Time-series material balance for $PM_{2.5}$ mass (from beta attenuation monitor [BAM] and tapered element oscillating microbalance [TEOM]), ammonium nitrate (1.29 × NO_3^- from R&P 8400N nitrate monitor), organic matter (1.4 × organic carbon from R&P ambient particulate carbon monitor), and elemental carbon (from R&P ambient particulate carbon monitor). Data acquired on 12/26/00 at Fresno.

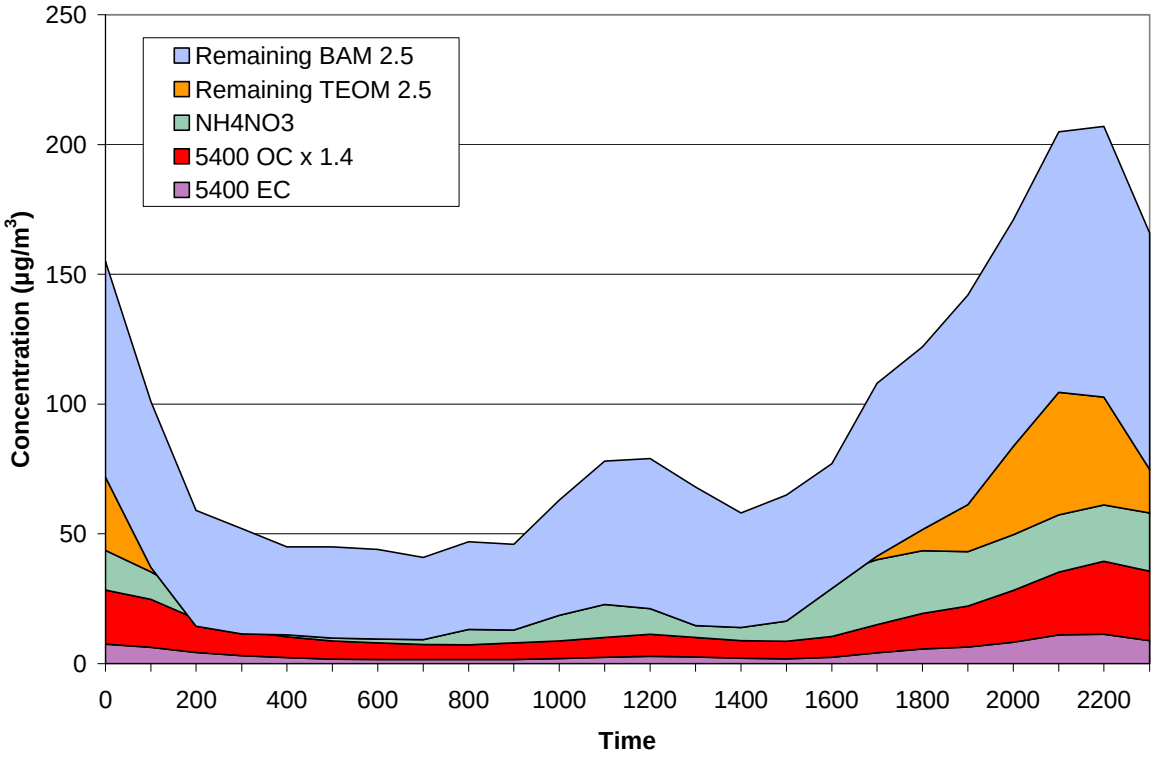
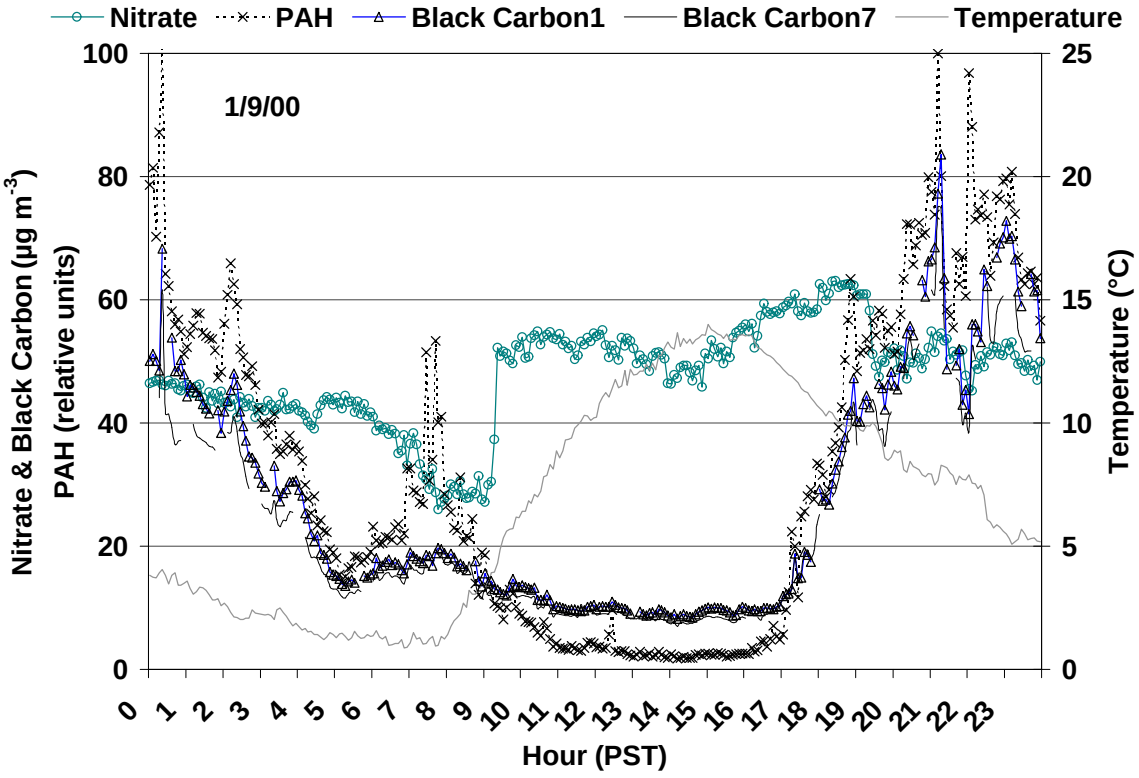


Figure 3.2-7. Diurnal changes in particle nitrate (10-minute), black carbon (5-minute, black carbon1 from single wavelength and black carbon7 from 880 nm channel of seven-wavelength aethalometers), particle-bound PAH (5-minute), and temperature (5-minute) on January 9, 2000.



decreased over a longer period surrounding the nitrate increase, from 4 μg/m^3 at 0840 PST to 2.5 μg/m^3 at 1025 PST. Five-minute averages for PAH, CO, and NO show intermittent spikes, indicative of pollutant wafts from nearby roadways or contributions from individual high-emitters. Black carbon concentrations show less spikiness than PAH, CO, or NO concentrations, indicating a more homogeneous source distribution or a longer time-constant in the signal detection. Black carbon is most abundant in diesel exhaust, wood burning, and cold-start or high-emitting gasoline vehicle emissions (e.g., Zielinska et al., 1998). Emissions inventories show CO and NO to be dominated by well-maintained gasoline vehicles operating in the hot-stabilized mode that have low black carbon emissions. There is not enough source information on photoionization PAH measurements to determine how they are related to different particulate carbon emitters.

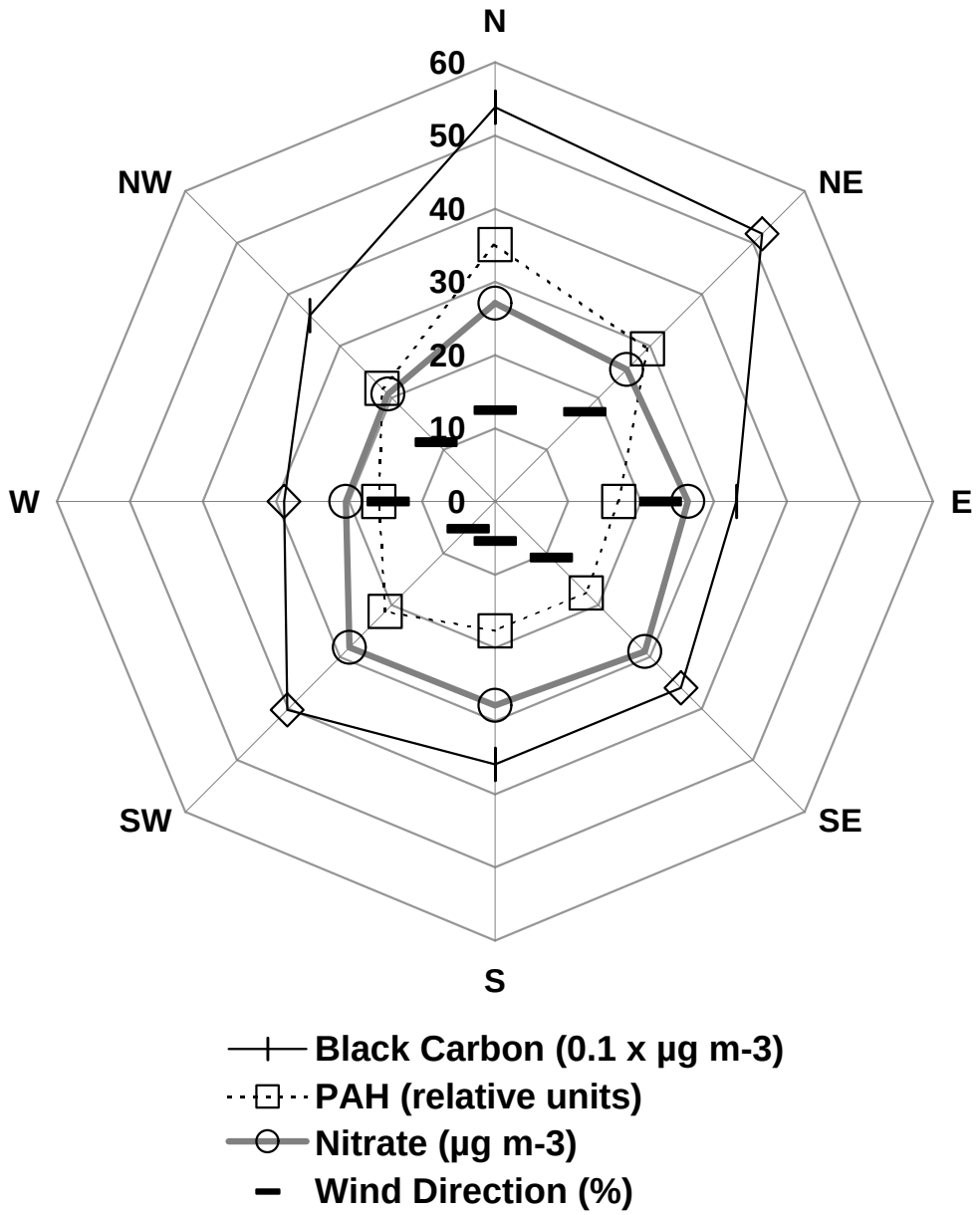
The afternoon measurements from the two aethalometers are practically identical, but the morning and evening measurements for the 880 nm channel of the seven-wavelength aethalometer were 75% to 85% of the single wavelength 880 nm values.

The changes in the ratio of PAH to black carbon throughout the day is also notable in Figure 3.2-7. The photoionization method for particle-bound PAH is reproducible, but at present it can only be related to absolute concentrations of particle-bound PAH via collocated filter samples. The ratio is often near unity, with notable spikes that are interpreted as very fresh (<5 minute aging) from nearby sources. After ~1000 PST, and until ~1800 PST, particle-bound PAH is substantially depleted with respect to black carbon in Figure 3.2-7, a phenomena that occurred on all days during winter 1999/2000. This is consistent with an aged aerosol that has undergone photochemical transformations (e.g., Chen et al., 2001). The ratio returned to unity, with short-duration pulses of higher ratios, into the evening.

Nitrate remained nearly constant throughout the afternoon, with a slight dip to 47 μg/m^3 as temperature approached its maximum of 14 °C at 1500 PST. Nitrate levels increased after 1500 PST as temperature decreased, achieving its highest concentration of 64 μg/m^3 at 1820 PST as the temperature dropped to 10 °C, then dropped to 48 μg/m^3 at 1930 PST and hovered at ~50 μg/m^3 for the rest of the day. The reason for the evening decrease in this case is not understood, although it corresponds to a short-term increase in wind speed that may have dispersed the cloud. The evening decrease is lower and over a longer period of time than the morning increase. This example demonstrates the need for chemically specific measurements at 5- to 10-minute resolutions. Even an hourly average would not capture the changes in this example.

Figure 3.2-8 shows the directionality of pollutant origins at Fresno for the first two weeks of January 2000. Transport was most frequent from the west, east, and northeast, and least frequent from the south and southwest. This contrasts with the prevailing northwesterly flows along the SJV axis that occur during other parts of the year. Black carbon and PAH levels were highest when transport was from the north and northeast, the direction of the southbound lane on First Street. These observables also have high values for the south and southwesterly direction, where highly traveled Shields Road is located. Nitrate concentrations did not show the same directionality, with average concentrations of

Figure 3.2-8. Pollution rose for the period of January 1 through 14, 2000. Average of 3,667 5-minute averages of black carbon and particle-bound PAH and 1,833 10-minute average nitrate concentrations for eight wind sectors. Also shown is the fraction of wind from each sector for this period. Missing black carbon measurements for the seven-wavelength aethalometer were replaced with those from the collocated single wavelength aethalometer. Only data records with valid measurements from all measurement systems are included in the averages.



~20 $\mu g/m^3$ from all directions except the east and northwest. This is further evidence that the markers for primary emissions are of urban origin whereas secondary nitrate is of regional origin.

$PM_{2.5}$ was low for most of the day on January 2 as a result of valleywide precipitation, but it built up rapidly as primary emissions accumulated in the evening. On January 12, the high morning concentrations decreased rapidly to low levels throughout the day with dissipation of both primary and secondary components, also due to atmospheric instability associated with precipitation. Pollution episodes do not correspond to the midnight beginning and end points of 24-hour samples. Even everyday samples are insufficient to fully understand the causes of excessive $PM_{2.5}$ and PM_{10} concentrations.

Spatial zones of influence vary as the study domain changes and the number of sampling sites included in the analysis increases. As shown in Figure 3.2-9, neighborhood-scale (8 km $\times$ 8 km) influences upon the two sites diminish when the geographical domain is extended to an urban scale (200 km $\times$ 200 km) to include 15 sites in the analysis. This type of sensitivity testing will be performed to determine an optimal number of sites.

More important questions for air quality monitoring are the frequency and measurement duration needed to identify, within a specified precision, the time of day of concentration maxima, or to measure the value of the peak concentration over a specified averaging time. Answers to these questions are directly relevant to designing appropriate monitoring efforts, whether for exposure assessment, air quality modeling, or routine compliance assessment.

Figure 3.2-9. Example of an average $PM_{2.5}$ contour plot from the winter 1999-2000 period showing concentration variations surrounding the Fresno site in a neighborhood-scale domain (8 km × 8 km, including 3 sites) as compared to an urban-scale domain (200 km × 200 km, including 15 sites).